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ABSTRACT

The Air Resources Board (ARB) conducted a canister comparison study to determine the effects of pressure, relative humidity, and canister residence time on non-methane hydrocarbon (NMHC) recovery rates from stainless steel canisters. The results of the study were used to support the photochemical assessment monitoring stations (PAMS) NMHC program and California's ambient toxics air monitoring program. The study was part of ARB's data accuracy evaluation to determine the best sampling conditions for compound recovery. As a result of the study, a protocol was established for the introduction of calibration, audit, and cleanliness samples to the analytical instrumentation. Compound recovery rates were not affected as a result of pressure, except when no humidity was present in the canister. The aromatic compound recovery rates increased as the canister pressure increased. Humidifying the canisters also improved the aromatic compound recovery rates, however, variations in the relative humidity above 18% showed no differences. Additionally, the canister residence time had no effect on the compound recovery rates. As a result of the study, ARB confirmed that the humidified canisters improved the recovery rates of aromatic compounds when analyzing calibration, audit, or cleanliness samples.

INTRODUCTION

In 1994, the ARB developed the NMHC laboratory audit program to evaluate the accuracy of ambient hydrocarbon data in California. While developing the audit program, questions arose regarding the effect various audit related factors (i.e., canister pressure, canister humidification, canister residence time) had on the accuracy of the results. Audit discrepancies were initially reported in blind audits of toxic compounds (particularly aromatics) that were conducted at field locations. To avoid a similar problem in the PAMS program, a canister comparison study was conducted to determine the effects of pressure, relative humidity, and canister residence time on NMHC recovery rates. The results of the study helped establish a protocol for introducing calibration, audit, and cleanliness samples to the analytical instrumentation. Cleanliness samples are a quality control check to verify that a batch of canisters are free from contamination prior to sampling.

Objectives

The objectives of the study were as follows: Determine the effect of canister pressure on compound recovery rates. Determine the effect of canister relative humidity on compound recovery rates. Determine the effect of residence time in the canister on compound recovery rates.

EXPERIMENT

Fourteen stainless steel Summa® passivated canisters were filled with a 56 component NMHC blend and subjected to various pressures and humidities (Table 1). The contents of the canisters were analyzed over a ten day period. The canisters were pressurized to 10, 20, and 30 pounds per square inch (psi) above ambient. Under normal sampling conditions, the laboratory evacuates sample canisters to -14.7 psi prior to field sampling, and the canisters return at a pressure of 10 psi above ambient. The laboratory routinely calibrates the analytical instrumentation using a humidified canister that has been pressurized with certified gas to 30 psi.

The canisters were humidified to 0, 18.1, 36.2, 72.4, and 100% by injecting specific amounts of high performance liquid chromatography grade water during the canisters' filling process. The relative humidities were calculated using the ideal gas law. The objective was to determine if pressure and humidity affected the recovery of the compounds, and if so, at what levels. The pressures and humidities used in the study were selected to determine the best sampling conditions for NMHC recovery given the constraints of the sampling and analysis processes.

The contents of each canister and the 56 component NMHC cylinder were analyzed for total NMHC using preconcentration direct flame ionization detection (PDFID) and speciation using flame ionization detection. Canister 1 was filled with nitrogen headspace to 10 psi, humidified to 100%, and analyzed as a laboratory blank sample. Canisters 2, 3, and 4 were filled to 10, 20, and 30 psi respectively with the gas blend, and a relative humidity of 0%. Canisters 5, 6, 7, and 8 were filled to 10 psi and relative humidities of 18.1, 36.2, 72.4, and 100% respectively. Canister 9 was filled to 20 psi and a relative humidity of 100%. Canisters 10, 11, 12, and 13 were filled to 30 psi and relative humidities of 18.1, 36.2, 72.4, and 100% respectively. Canister 14 was a repeat of canister 12. Prior to and after analyzing the contents of the canisters, the contents of the cylinder used to fill the canisters were analyzed by direct injection into the analytical instrumentation. The direct injection results were used as the baseline for each compound to determine if conditions within the canisters affected the recovery rates. Additionally, the results from each canister were compared to each other with respect to time to determine if sample degradation occurred. The contents of the canisters were analyzed four times over a ten day period.

Quality Control

To ensure the precision of the study data, the QAS followed standard laboratory quality control practices. A custom multi-gas blend cylinder used to determine retention times for the PAMS program was used as the reference. The cylinder had assigned values for each compound. Canister 1 was filled with nitrogen headspace to 10 psi, humidified to 100%, and analyzed as a blank, emulating field and laboratory conditions. The laboratory's standard operating procedures were followed. All of the canisters were verified as clean prior to being used in the study, whereas the normal protocol requires 10% of the canisters be checked. The cleanliness criteria used to check the canisters were as follows:

<u>Contaminant</u>	<u>NMHC Criteria Level (pphmC)</u>
Speciated - per component	0.1

EXPERIMENT RESULTS

The results of the study showed that canister pressure and humidity did affect the compound recovery rates. The total NMHC data indicated that canisters 2 and 3 (10 and 20 psi, 0% relative humidity) had recovery rates significantly lower than the recovery rates by direct injection. In general, compound recovery rates increased with an increase in canister pressure. Canister 4, which had a pressure of 30 psi and a relative humidity of zero, had a recovery rate equal to that of the humidified canisters (canisters 5 through 14) and the reference cylinder analyzed by direct injection (Figure 1). The recovery rates from the humidified canisters for total NMHC were equal to the results by direct injection. There were also no differences in the recovery rates among the humidified canisters. Variations in the canister's relative humidity (18.1, 36.2, 72.4, and 100%) and the canister residence time did not affect the total NMHC recovery rates. The speciated NMHC data indicated that changes in the canister's pressure and relative humidity above 18% had no effect on the recovery rates of the alkane and alkene compounds. Changes in the pressure and humidity did affect the recovery rates of the aromatic compounds. At zero humidity, the aromatic compound responses were significantly lower than the direct injection responses. However, at zero humidity the recovery rates improved with an increase in the pressure. With humidity greater than 18%, speciated NMHC recovery rates were equal to the direct injection results (Figure 2). Variations in the canisters' relative humidity (18.1, 36.2, 72.4, and 100%) and the canister residence time did not affect the speciated NMHC recovery rates. The speciated NMHC data further indicated that the percent difference from the assigned values correlated with the type of compound analyzed (alkane, alkene, aromatic). Using the assigned values, the percent differences were calculated for the canister and direct injection recovery rate data. In general, the alkane compounds percent differences from the assigned values ranged from 0 to -5%, the alkenes ranged from -5 to -10%, and the aromatics ranged from -10 to -30% (Table 2). The relationship between the low recovery rates and the type of compound was not attributed to the effects of humidification, pressure, and canister residence time.

CONCLUSIONS

The objectives of the canister comparison study were to determine if pressure, relative humidity, and canister residence time effected the NMHC recovery rates from stainless steel canisters. The study concluded that: Canister pressure affected the aromatic compound recovery rates when zero humidity was present. As the canister pressure increased from 10 to 30 psi, the aromatic compound recovery rates increased. Humidified canisters increased the aromatic compound recovery rates. Variations in the canister relative humidity above 18% had no effect on the compound recovery rates. Canister residence time up to ten days had no effect on the compound recovery rates. In addition to the objectives of the study, the study indicated that a compound's percent difference from the assigned value was related to the type of compound being analyzed. In general, the canister and direct injection compound recovery rates were comparable to the assigned values for the alkane compounds. However, the alkene compounds recovery rates showed slightly lower results and the aromatic compounds showed a significant difference.

RECOMMENDATIONS

Laboratories conducting NMHC analyses should humidify the canisters when introducing audit, calibration, and cleanliness samples to the analytical instrumentation. Humidifying audit and calibration samples is essential. Humidifying cleanliness samples will allow laboratory staff to detect contaminated canisters when aromatic compounds exceed 0.1 pphmC. Laboratories should also continue to investigate possible causes for the lower recovery rates of alkene and aromatic compounds.

CANISTER CONDITIONS

Table 1. Canister Pressures and Humidities

CANISTER #1 Pressure - 10 psi Humidity - 100%	CANISTER #8 Pressure - 10 psi Humidity - 100%
CANISTER #2 Pressure - 10 psi Humidity - 0.0	CANISTER #9 Pressure - 20 psi Humidity - 100%
CANISTER #3 Pressure - 20 psi Humidity - 0.0	CANISTER #10 Pressure - 30 psi Humidity - 18.1%
CANISTER #4 Pressure - 30 psi Humidity - 0.0	CANISTER #11 Pressure - 30 psi Humidity - 36.2%
CANISTER #5 Pressure - 10 psi Humidity - 18.1%	CANISTER #12 Pressure - 30 psi Humidity - 72.4%

CANISTER #6	CANISTER #13
Pressure - 10 psi Humidity - 36.2%	Pressure - 30 psi Humidity - 100%
CANISTER #7	CANISTER #14
Pressure - 10 psi Humidity - 72.4%	Pressure - 30 psi Humidity - 72.4%

NOTE: Canister #14 was a repeat of Canister #12.

CANISTER COMPARISON STUDY RESULTS

Table 2. Compound Percent Difference From Assigned Value

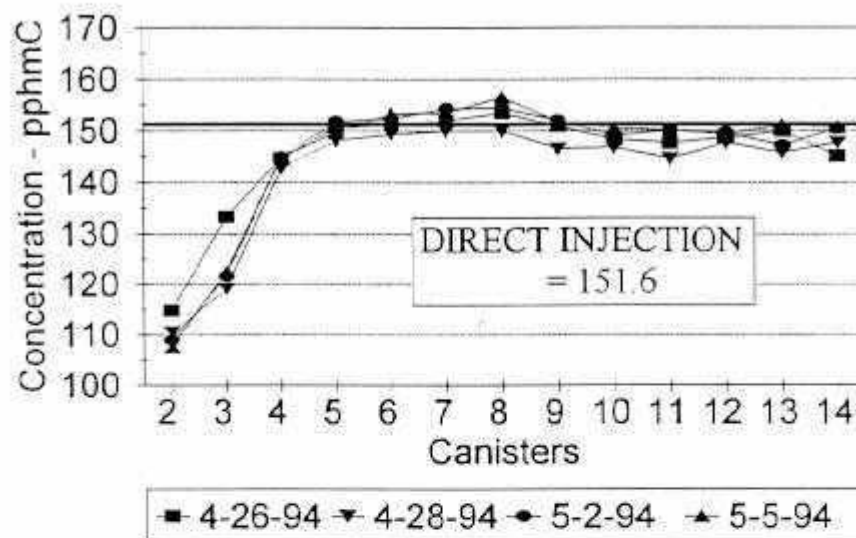
<u>COMPOUND</u>	<u>PERCENT DIFFERENCE</u>	<u>COMPOUND</u>	<u>PERCENT DIFFERENCE</u>
Ethane	0.0	Methylcyclopentane	-1.6
	-5.3		-3.1
Ethene	-2.5	2,4-Dimethylpentane	-11.0
	-9.7		-3.5
Propane	-5.3	Benzene	1.3
	-2.2		15.8
Propene	-49.7	Cyclohexane	1.9
	-2.8		0.0
Isobutane	-7.2	2-Methylhexane	-1.9
	-7.8		-3.1
Butane	-8.4	2,3-Dimethylpentane	-0.6
	-1.3		-7.8
Ethyne	-6.3	3-Methylhexane	-1.3
	-1.6		0.0
t-2-Butene	-16.0	2,2,4-Trimethylpentane	-1.3
	-4.3		-14.4
1-Butene	-5.0	Heptane	-20.1
	-18.8		-57.2
c-2-Butene	-2.2	Methylcyclohexane	-13.8
	-9.1		-8.5
3-Methylbutene	-3.5	2,3,4-Trimethylpentane	-17.3
	-5.9		-32.4
2-Methylbutane	-2.2	Toluene	-55.2
	1.6		-18.4
1-Pentene	0.0	2-Methylheptane	-20.1
	-88.7		-23.9

Pentane	-0.3	3-Methylheptane	-70.1
Isoprene	-5.3		
t-2-Pentene	-2.2	Octane	
c-2-Pentene		Ethylbenzene	
2-Methyl-2-Butene		m/p-Xylene	
2,3-Dimethylbutane		Styrene	
Cyclopentene		o-Xylene	
4-Methylpentene/		Nonane	
3-Methylpentene		Iso-Propylbenzene	
Cyclopentane		alpha-Pinene	
2,3-Dimethylbutane		n-Propylbenzene	
2-Methylpentane		1,3,5-Trimethylbenzene	
3-Methylpentane		1,2,4-Trimethylbenzene	
2-Methylpentene		Decane	
Hexane		beta-Pinene	
t-2-Hexene			
c-2-Hexene			

COMMENTS: Canister Condition - 10 psi, 100% Relative Humidity Percent
Difference = [(Measured Value - Assigned Value)/Assigned Value] x 100

TOTAL NMHC

PDFID



TOTAL NMHC

SUM OF SPECIES

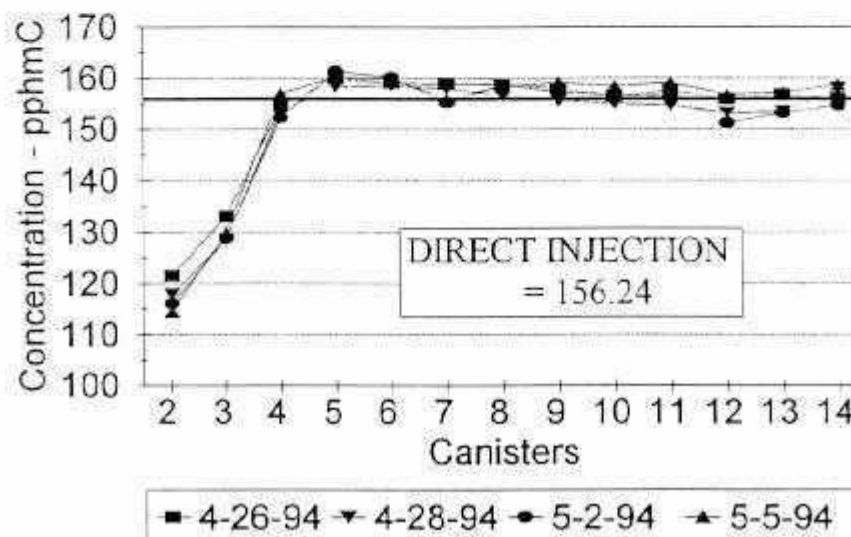


Figure 1. Data Comparison for Total NMHC.

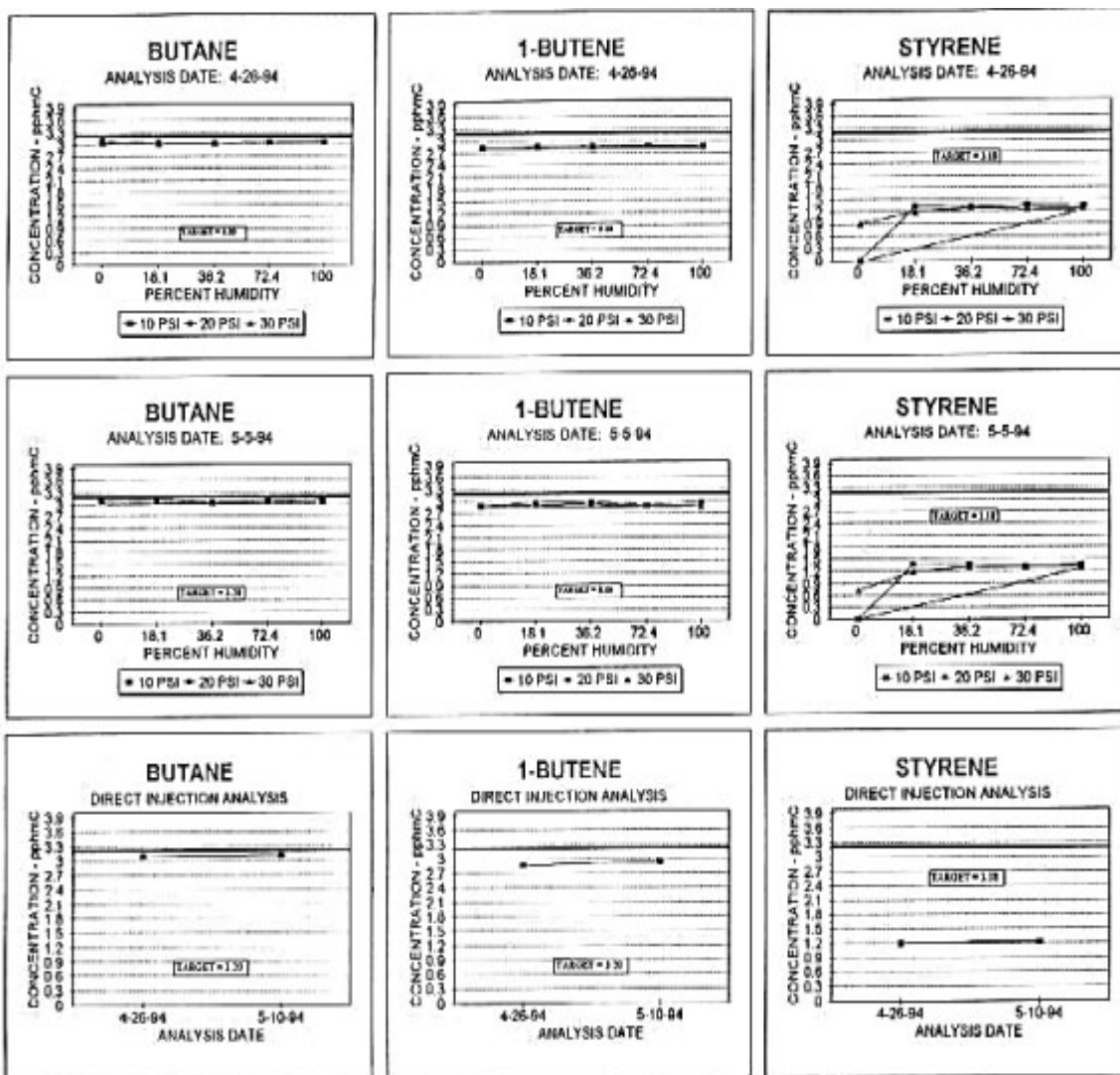


Figure 2. Data Comparison for Speciated NMHC